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TITLE OF INVENTION : Heat-shrinkable Co-extruded Polyethylene Film

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Abstract

[Object] To provide a heat-shrinkable co-extruded polyethylene film that has impact resistance and high tensile modules which is suitable for high speed packaging.

[Constitution] A film having a tensile modulus of higher than $4,000 \text{ kg/cm}^2$ and impact strength of higher than 6 kg.cm can be obtained by biaxially stretching a co-extruded film comprising a middle layer made from a low density linear polyethylene (A) 50 - 90 weight % having $d = 0.900 - 0.930 \text{ g/cm}^3$ and $\text{MI} = 0.3 - 5.0 \text{ g/10 minutes}$ and a cyclolefin resin (B) 10 - 50 weight % comprising mainly of low density cyclolefin resin (B) which has $T_g \geq 50^\circ\text{C}$ and is an ethylene/cyclolefine random copolymer, and an innermost layer and an outermost layer made mainly of a low density linear polyethylene (C) having $d = 0.900 - 0.930 \text{ g/cm}^3$ and $\text{MI} = 0.5 - 3.0 \text{ g/10 minutes}$. Furthermore, heat resistance and packaging finish can be improved by crosslinking the film using electron beam having a dose of 1 - 10 Mrad.

Claims

[Claim 1] A heat-shrinkable co-extruded polyethylene film having a tensile modulus of 4000 g/cm^2 or higher and comprising middle layer having a middle layer, innermost layer and outermost layer, where the middle layer is made of a low density linear polyethylene (A) 50 - 90 weight % having a density of $0.900 - 0.930 \text{ g/cm}^3$ and a melt index of $0.3 - 5.0 \text{ g/10 minutes}$ and a cyclolefin resin (B) 10 - 50 weight % comprising mainly an ethylene/cyclolefin random copolymer made of a copolymer of ethylene and cyclolefin, and the innermost layer and outermost layer are made of a composition that contains a low density linear polyethylene (C) having a density of $0.900 - 0.930 \text{ g/cm}^3$ and melt index of $0.5 - 3.0 \text{ g/10 minutes}$ as its major component.

[Claim 2] The heat-shrinkable co-extruded polyethylene film acquired by crosslinking the heat-shrinkable co-extruded polyethylene film described in Claim 1, using electron beam having a dose of 1 - 10 Mrad.

Comprehensive explanation of invention

[0001]

[Field of commercial utility]

This invention relates to a heat-shrinkable co-extruded polyethylene film, and particularly to a heat-shrinkable co-extruded polyethylene film which is highly adaptable to a high speed packaging machine.

[0002]

[Prior art]

Traditionally, polyvinylchloride film, polyethylene film and polypropylene film have been known as the heat-shrinkable packaging material. Heat-shrinkable polyethylene and polypropylene films are used favorably because they are inexpensive and can be disposed easily after use. Among them, the heat-shrinkable polyethylene film is attracting a particular attention because its has excellent impact resistance and heat-sealing strength, and thus it is expected to be useful in many areas.

[0003]

[Problems to be solved by invention]

In case of using a heat-shrinkable polyethylene film as the packaging material for use in an automatic packaging machine, packaging can be made fairly easily if the packaging speed is relatively slow. However, like in the modern practice of running the process at an extremely high packaging speed, it tends to cause problems such as a running trouble or heat-sealing troubles caused by shift of cutting pitch. Adaptability to high speed packaging machine is related to the strength of the film which is expressed also by the tensile modulus of the film. Running trouble or shift of cutting pitch during high speed packaging is believed to be caused by the low tensile modulus of the film being used as the packaging material. Therefore, it is desirable to have a packaging material made of heat-shrinkable polyethylene film that has an excellent impact resistance and also has a high tensile modulus suitable for high speed packaging.

[0004]

Now, heat-shrinkable film made of cyclolefin resin has been disclosed in Japanese Kokai Patent HEI 2-196832 (1990) and Japanese Kokai Patent HEI 5-262899(1993).

However, even though the heat-shrinkable film disclosed in Japanese Kokai Patent HEI 2-196832 (1990) may have a high modulus, its impact resistance is inferior to the heat-shrinkable polyethylene film. And, the heat-shrinkable film disclosed in

Japanese Kokai Patent HEI 5-262899 (1993) does not have a high tensile modulus because its transition temperature is lower than 30°C, and therefore it is inferior in its adaptability to the high speed packaging machine.

[0005]

[Means to solve the problems]

As a result of an extensive study to search for a heat-shrinkable film that does not have the above-said flaws, the present inventors have finally arrived at this invention. Thus, this invention intends to provide a heat-shrinkable co-extruded polyethylene film having a tensile modulus of 4000 kg/cm² or higher and is made of a middle layer, innermost layer and outermost layer, where the middle layer is made of a low density linear polyethylene (A) 50 - 90 weight % having a density of 0.900 - 0.930 g/cm³ and a melt index of 0.3 - 5.0 g/10 minutes and a cycloolefin resin (B) 10 - 50 weight % made of an ethylene/cycloolefin random copolymer which is made of a copolymer of ethylene and cycloolefin, and the innermost layer and outermost layer are made of a composition where the major component is a low density polyethylene (C) having a density of 0.900 - 0.930 g/cm³ and a melt index of 0.5 - 3.0 g/10 minutes. Furthermore this invention intends to provide a heat-shrinkable co-extruded film formed by crosslinking the above-said film, using electron beam having a dose of 1 - 10 Mrad.

[0006]

This invention is explained comprehensively in the following. The low density linear polyethylene (A) to be used in this invention has a density of 0.900 - 0.930 g/cm³ at 25°C and a melt index of 0.3 - 5.0 g/10 minutes. And, a density of 0.910 - 0.925 g/cm³ and a melt index of 0.5 - 3.0 g/10 minutes are preferred. A density of lower than 0.900 g/cm³ is not desirable because it will lower then tensile modulus. And, a density of higher than 0.930 g/cm³ is not desirable because the shrinkability at lower temperature is not favorable. And, a melt index of less than 0.3 g/10 minutes is not desirable because it will raise the load on the motor during the melt extrusion work. And, a melt index of higher than 5.0 g/10 minutes is not desirable because it tends to worsen the stability during the stretching process. Preferred α -olefins that can be used to copolymerize with the ethylene in the low density linear polyethylene are one, two or more α -olefins selected from a group comprising butene-1, pentene-1, hexene-1-, heptene-1, octene-1, 4-methylpentene-1 and so on.

[0007]

The cyclolefin resin (B) to be used in this invention is the ethylene/cyclolefin random copolymers made of the copolymer of ethylene and cyclolefins, and those which have a glass transition temperature of 50°C or higher, preferably 70°C or higher, are used. A glass transition temperature of lower than 50°C is not desirable because a high tensile modulus can not be obtained.

[0008]

The cyclolefin resin (B) to be used in this invention contains 52 - 90 mol %, preferably 55 - 80 mol %, of the structural unit derived from ethylene and 10 - 48 mol %, preferably 20 - 45 weight %, of the structural unit derived from cyclolefin, and any of the known cyclolefin resins comprising such constituents can be used. Examples of the cyclolefins are bicyclo[2,2,1]hepto-2-ene derivatives, tetracyclo[4,4,0,1^{3,5},1^{7,10}]-3-dodecene derivatives, hexacyclo[6,6,1,1^{3,6},1^{10,13},0^{2,7},0^{9,14}]-4-heptadecene derivatives, octacyclo[8,8,0,1^{2,6},1^{4,7},1^{11,13},1^{13,16},0^{3,8},0^{12,17}]-5-dococene derivatives, pentacyclo[6,6,1,1^{3,6},0^{2,7},0^{9,14}]-hexadecene derivatives, heptacyclo-5-eicocene derivatives, heptacyclo-5-heneicocene derivatives, tricyclo[4,3,0,1^{2,5}]-3-decene derivatives, tricyclo[4,3,0,1^{2,6}]-3-undecene derivatives, pentacyclo[6,5,1,1^{3,6},0^{2,7},0^{9,13}]-4-pentadecene derivatives, pentacyclopentadecadiene derivatives, pentacyclo- [7,4,0,1^{2,5},1^{9,12},0^{8,12}]-pentadecene derivatives, pentacyclo[8,7,0,1,3,6,1^{10,17},1^{12,13},0^{2,7},0¹¹⁻¹⁵]-4-eicocene derivatives, nonacyclo[10,9,1,1^{4,7},1^{13,20},1^{15,18},0^{3,8},0^{2,10},0^{12,21},0^{14,19}]-5-pentacocene derivatives, pentacyclo[8,4,0,1^{2,3},1^{9,12},0^{8,13}]-3-hexadecene derivatives, pentacyclo[8,4,0,1^{4,7},10^{11,18},10^{13,16},0^{3,8},0^{12,17}]-5-heneicocene derivatives, nonacyclo[10,10,1,1^{5,8},1^{14,21},1^{15,19},0^{3,11},0^{4,9},0^{13,22},0^{15,20}]-5-hexacocene derivatives, 1,4-methano-1,4,4a,5,10,10a-hexahydroanthracene derivatives, cyclopentadiene-acenaphthylene adducts and so on. Cyclolefin resins can be prepared by the methods described, for example, in Japanese Kokai Patent SHO 60-168708(1985), Japanese Kokai Patent SHO 61-120816 (1986), Japanese Kokai Patent SHO 61-115912 (1986), Japanese Kokai Patent SHO 61-115916 (1986), Japanese Kokai Patent SHO 61-271308 (1986), Japanese Kokai Patent SHO 61-272216 (1986), Japanese Kokai Patent SHO 62-252406 (1987), and Japanese Kokai Patent SHO 62-252407 (1987), and so on.

[0009]

Amount of the low density linear polyethylene (A) to be used as a component of the middle layer in this invention is 50 - 90 weight %, preferably 55 - 85 weight %. And, 60 - 80 weight % is even more desirable. And, the amount of cyclolefin resin (B) to

be used as the other component is 50 - 10 weight %, preferably 45 - 15 weight %. And, 40 - 20 weight % is even more desirable. If the amount of low density linear polyethylene (A) being used is less than 50 weight %, it tends to lower the transparency, gloss and impact resistance and therefore it is not desirable. And, if the amount exceeds 90 weight %, it tends to lower the tensile modulus, which is not desirable.

[0010]

And, other resins such as high pressure polyethylene, ethylene/vinyl acetate copolymer, ionomer, and propylene/butene copolymer may be used together in the middle layer as long as it does not interfere with the purpose of this invention.

[0011]

In this invention, the middle layer does not have to be only one layer, and two or more layers may be provided, if necessary. For example, a layer made of the resin having high gas barrier property may be used as another middle layer, to improve the gas barrier property. Thickness of the middle layer must be more than 30% of the entire layer. If it is less than 30%, high tensile modulus can not be obtained.

[0012]

Low density linear polyethylenes having a density of 0.900 - 0.930 g/cm³ and a melt index of 0.5 - 3.0 g/10 minutes can be used as the low density linear polyethylene (C) in the innermost layer and outermost layer of this invention. And, preferred density is 0.910 - 0.925 g/cm³ and preferred melt index is 0.8 - 2.0 g/10 minutes. A density of lower than 0.900 g/cm³ is not desirable because it tends to lower the slidability. On the other hand, a density of higher than 0.930 g/cm³ is not desirable because it tends to lower the transparency and gloss. And, a melt index of less than 0.5 g/10 minutes is not desirable because it tends to lower the transparency and gloss, and a melt index of higher than 3.0 g/10 minutes is not desirable because it lowers the heat sealing strength. Incidentally, the type of low density linear polyethylene (C) may be the same as the low density linear polyethylene (A) being used in the middle layer.

[0013]

And, thickness of the innermost layer and outermost layer made of the low density linear polyethylene (C) is at least 1 μ m or more, preferably 2 μ m or more. If the thickness of the innermost layer and outermost layer is less than 1 μ m, it tends to lower the transparency, gloss and heat-sealing strength, which is not desirable.

[0014]

And, ethylene/vinyl acetate copolymers, ethylene/ α -olefin copolymers, propylene/butene copolymers, ionomers, polybutene, etc. can be used in the innermost layer and outermost layer, as long as it does not interfere with the purpose of this invention.

And, if so desired, additives such as lubricant, blocking inhibitor, antistatics, fog inhibitor and so on may be used, respectively. This will be effective when such additive(s) is added in the innermost layer and outermost layer.

[0015]

Furthermore, a heat-shrinkable co-extruded polyethylene film which has been crosslinked by using electron beam having a dose of 1 - 10 Mrad, preferably 3 - 7 Mrad, is provided by this invention. A dosage of less than 1 Mrad is not desirable because it can not improve the heat resistance. And, a dosage of higher than 10 Mrad is not desirable because it tends to lower the heat sealability. The heat-shrinkable co-extruded polyethylene film which has been crosslinked under such condition has an improved heat resistance. Therefore, the shrinking tunnel temperature during the shrink packaging can be set higher for such film, and a beautiful packaging finish can be created. Therefore, such film is suitable for shrink-pack the bottles for cosmetics and shrink-pack the article that has a complicated shape, beautifully.

[0016]

Method of preparation of the film of this invention is indicated in the following. Any publicly known methods can be used as the method to prepare the stretched film of this invention using the above-said resin. An example of preparation of a trilayer laminated tubular film by drawing is explained in the following. First, the compositions made of the above-said low density linear polyethylene (A) and cycloolefin resin (B) is used to form the middle layer and a low density linear polyethylene (C) is used to form the innermost layer and outermost layer, by melting and blending in three respective extruders, and they are co-extruded in tubular form from trilayer circular dies, and quenched and solidified without stretching, to form a tubular unstretched film.

[0017]

The thus-obtained tubular unstretched film is fed into a tubular stretching apparatus illustrated in Fig. 1, for example. A gas pressure is applied to the interior of the tube at a highly orientable temperature range, such as 10°C lower than the

melting point of the resin in the middle layer, preferably 15°C lower than the melting point, to cause biaxial orientation simultaneously by expansion and stretching. The stretching ratio in the longitudinal direction does not have to be the same as the lateral direction. However, in order to acquire a desirable property such as excellent strength and shrinkage ratio, etc., it is desirable to stretch 2-folds or more, preferably 2.5-folds or more, and even more desirably 3-folds or more, in both longitudinal and lateral directions. The film taken out of the stretching apparatus may be annealed, if so desired. With annealing, natural shrinkage during storage can be suppressed.

[0018]

For crosslinking, the tubular unstretched film is irradiated from both sides of the tube with electron beam having a dose of 1 - 10 Mrad. Later, the tube is stretched by the method similar to the one described above, to obtain a crosslinked heat-shrinkable co-extruded polyethylene film.

[0019]

[Fig. 1]

[0020]

[Examples]

This invention is explained embodimentally by the following examples which, however, are not intended to limit the scope of this invention. Incidentally, following methods were used to determine the properties shown in these examples.

- (1) Haze : Haze was determined by the procedure specified in JIS-K6714.
- (2) Gloss (60°C) : Gloss was determined by the procedure specified in JIS-Z8741.
- (3) Tensile modulus : Tensile modulus was determined by the procedure specified in JIS-K7127.
- (4) Impact strength : Impact strength was determined by the procedure specified in JIS-P8134.
- (5) Adaptability to high speed packaging machine : Using a automatic packaging machine (model PW-R2, a pillow type packaging machine, manufactured by Tokiwa Kogyo K.K.), cupped ramen (dry noodle) was packaged at a speed of

150 packages/minutes (about 36 m/minute), and the condition of packaging was examined.

[0021]

Example 1

A low density linear polyethylene having a density of 0.920 g/cm³ and a melt index of 1.0 g/10 minutes was used for the inner layer and outer layer. And, a mixture made of 85 weight % of the same low density linear polyethylene as the inner and outer layer and 15 weight % of the cyclolefin copolymer (APL6509, a product of Mitsui Petrochemical K.K., glass transition point = 80°C) was used for the middle layer. Using three extruders, they were molten and blended, respectively, at 170 - 240°C. The amount to be extruded by each extruder was set in such a way that the ratio of the thickness of each layer would be (inner layer : middle layer : outer layer) = 1 : 5 : 1, and they were co-extruded downward from a trilayer circular dies kept at 240°C. The thus-formed tube made of three layers was allowed to move through a cylindrical cooling mandrel, while moving the outer surface of the mandrel whose interior was circulated with cold water, to cool and reel in the tube. Thus, an unstretched film having a diameter = 75 mm and thickness = 320 µm was obtained. This unstretched tubular film was guided to a tubular biaxial stretching apparatus illustrated in Fig. 1, and it was stretched 4-folds in each of the longitudinal and lateral directions at 90 - 110°C, to obtain a heat-shrinkable co-extruded polyethylene film having a thickness of about 20 µm. Then, after heating this stretched film in a tubular annealing apparatus with hot air at 75°C for 10 seconds, it was cooled down to room temperature, folded and reeled. During the stretching process, the film remained stable. There were no up-down movement at the stretching point and no shaking of the stretching tube. And, there was no heterogeneously stretched state such as necking. The thus-obtained stretched film, as indicated in Table 1, showed excellent transparency and gloss, and had high tensile modulus and impact strength. Even in the packaging evaluation using a pillow type packaging machine, there were no running trouble and no heat-sealing trouble, and thus it showed excellent adaptability to a high speed packaging machine.

[0022]

Example 2

Materials and procedure of the Example 1 were employed, except changing the mixing ratio of the middle layer to low density linear polyethylene = 55 weight % and cyclolefin copolymer = 45 weight %, to prepare a heat-shrinkable co-extruded

polyethylene film. The thus-obtained stretched film, as indicated in Table 1, showed excellent transparency and gloss, and also high tensile modulus and impact strength.

Even in the packaging evaluation using a pillow type packaging machine, there was no running trouble nor heat sealing trouble, and thus it showed excellent adaptability to a high speed packaging machine.

[0023]

Example 3

Low density linear polyethylene having a density of 0.920 g/cm^3 and a melt index of 1.0 g/10 minutes was employed as the inner and outer layers, and the mixture made of 70 weight % of low density linear polyethylene (density - 0.916 g/cm^3 , melt index = 1.2 g/10 minutes) and 30 weight % of cyclolefin copolymer (product of Mitsui Petrochemical K.K., glass transition point = 80°C) was employed as the middle layer), to prepare a heat-shrinkable co-extruded polyethylene film by the procedure of Example 1. The thus-obtained stretched film, as indicated in Table 1, showed excellent transparency and glass, and had high tensile modulus and impact strength. In the packaging evaluation using a pillow type packaging machine, there was no running trouble nor heat-sealing trouble, and thus it had an excellent adaptability to a high speed packaging machine.

[0024]

Example 4

The unstretched film (thickness = $320 \mu\text{m}$) obtained in Example 3 was employed to run crosslinking treatment at a dosage of 5 Mrad, using an electron beam irradiator (manufactured by Nisshin High Voltage K.K.). Then, this tubular unstretched film was stretched by the method of Example 1, to prepare a heat-shrinkable co-extruded polyethylene film. The thus-obtained stretched film, as indicated in Table 1, showed excellent transparency and gloss and had high tensile modulus and impact strength. Even in packaging evaluation using a pillow type packaging machine, there was no running trouble nor heat-sealing trouble, and thus it showed excellent adaptability to a high speed packaging machine. Even when the temperature setting of the shrinking tunnel was raised to improve the heat resistance in the crosslinking treatment, the film did not burn (whitening or rupture caused by melting), and thus the finish of the package was beautiful.

[0025]

Comparative Example 1

Heat-shrinkable co-extruded polyethylene film was prepared by the procedure of Example 1, using a low density linear polyethylene (density = 0.920 g/cm^3 , melt index = 1.0 g/10 minutes) as the inner layer and outer layer and using 100 weight % of the low density linear polyethylene (the one identical to those used in inner and outer layer) as the middle layer. The thus-obtained stretched film, as indicated in Table 1, had excellent transparency, gloss and impact strength. In packaging evaluation using a pillow type packaging machine, it showed an excellent adaptability to the packaging machine up to the packaging speed of 50 pieces/minute (about 12 m/minute) However, when the packaging speed was raised to 150 pieces/minutes (about 36 m/minute), running trouble caused by snaking of the film and heat-sealing trouble caused by shifting of the cutting pitch occurred frequently because it had a low tensile modulus.

[0026]

Comparative Example 2

A heat-shrinkable co-extruded film was prepared by the procedure of Example 1, by employing the low density linear polyethylene (density = 0.920 g/cm^3 , melt index = 1.0 g/10 minutes) as the surface layer, and a mixture of 40 weight % of the low density linear polyethylene (same as the surface layer) and 60 weight % of a cyclolefin copolymer (a product of Mitsui Petrochemical K.K., glass transition point = 80°C) as the middle layer. The thus-acquired stretched film, as indicated in Table 1, showed high tensile modulus. In the packaging evaluation using a pillow type packaging machine, it showed excellent adaptability to the packaging machine, but it showed poor transparency and gloss and extremely low impact strength.

[0027]

			Examples				Comparative Examples	
			1	2	3	4	1	2
Feedstock protocol	Surface layer	Resin composition	LLDPE	LLDPE	LLDPE	LLDPE	LLDPE	LLDPE
	Middle layer	Resin composition	A:LLDPE B:(*)	A:LLDPE B: (*)	A:LLDPE B: (*)	A:LLDPE B: (*)	A:LLDPE B: (*)	A:LLDPE B: (*)
		Mixing ratio	A : B 85:15	A : B 55:45	A : B 70:30	A : B 70:30	A : B 100:0	A : B 40:60
Haze (%)			3.2	4.1	3.5	3.4	3.0	5.2
Gloss (%)			138	132	136	136	138	125
Tensile modulus (kg/cm ²)		MD	4300	7900	5600	5600	2800	8500
		TD	4400	7700	5300	5400	2700	8500
Impact strength (kg.cm)			7.9	6.3	7.3	7.5	8.0	4.7
Adaptability to high speed packaging machine			0	0	0	0	x	0

* Resin in the middle layer B.....Cyclic olefin copolymer.

[Effect of invention]

Compared to the conventional heat-shrinking polyethylene film, the film of this invention whose innermost layer and outermost layer are made of a low density linear polyethylene resin and the middle layer is made of a mixture of low density linear polyethylene resin and cyclolefin resin at a certain mixing ratio, has high tensile modulus. Thus, it is a packaging material with excellent adaptability to a high speed packaging machine. Therefore, it is free of running trouble or heat-sealing trouble caused by shifting of the cutting pitch during the packaging process in an automatic high speed packaging machine. Furthermore, since the film crosslinked by electron beam irradiation has an improved heat resistance, it is suitable for shrink-pack an article that has a complicated shape in a beautiful manner.

Brief explanation of drawing

[Fig. 1] Fig. 1 is a brief cross-sectioned view of the tubular biaxial stretching apparatus being used in the illustrated example.

- 1.....Unstretched film
- 2.....Low speed nip roll
- 3.....High speed nip roll
- 4.....Auxiliary heater
- 5.....Main heater
- 6.....Air cooling
- 7.....Folding rolls

Fig. 1



